

OXIDATION OF POLYCYCLIC AROMATIC HYDROCARBONS BY FENTON REACTION

OXIDACE POLYCYKlickÝCH AROMATICKÝCH UHLOVODÍKŮ FENTONOVOU REAKCÍ

Petra MALÍKOVÁ¹, Jitka HAJDUKOVÁ², Lucie NEZVALOVÁ³

¹ Ing., Faculty of Mining and Geology, VŠB – Technical University of Technology
17. listopadu 15, Ostrava - Poruba, tel. (+420) 59 732 9382
e-mail: petra.malikova@vsb.cz

² Ing., Faculty of Mining and Geology, VŠB – Technical University of Technology
17. listopadu 15, Ostrava - Poruba, tel. (+420) 59 732 9382
e-mail: jitka.hajdukova@vsb.cz

³ Ing., Faculty of Mining and Geology, VŠB – Technical University of Technology
17. listopadu 15, Ostrava - Poruba, tel. (+420) 59 732 5188
e-mail: lucie.nezvalova.st1@vsb.cz

Abstract

The paper deals with the oxidizing process (Fenton reaction) at degradation of organic pollutants from stream sediment. Oxidation was performed on sediments from the Černý příkop locality, which run through Ostrava Mariánské hory. It is location, which is negatively affected by industrial activities. The Fenton reaction is an oxidation reaction, when hydrogen peroxide as an oxidizer is used. First part of the experiment was the determination of an optimum dose of concentrated hydrogen peroxide. In the second part the effect of time and hydrogen peroxide concentration was examined on efficiency of the Fenton reaction.

Abstrakt

Článek pojednává o oxidaci polycyklických aromatických uhlovodíků Fentonovou reakcí. Oxidace byla provedena na sedimentech z lokality Černý příkop, který protéká Ostravou Mariánské hory. Jedná se o lokalitu, která je negativně ovlivněna vlivem průmyslové činnosti. Použitá Fentonova reakce je oxidační reakce, kdy se jako oxidační činidlo používá peroxid vodíku. První část experimentu se skládala, ze stanovení optimální dávky koncentrovaného peroxidu vodíku. Ve druhé části se pak zkoumal vliv času a koncentrace peroxidu vodíku na účinnost Fentonovy reakce.

Key words: polycyclic aromatic hydrocarbons, Fenton reaction, sediments, Černý příkop, hydrogen peroxide.

1 INTRODUCTION

Polycyclic aromatic hydrocarbons are organic compounds consisted of two or more condensed benzene nuclei in linear, angular or cluster arrangements. For their long-term ability to persist in the environment and health severity (they reveal carcinogenic and mutagen effects) they are treated as typical representatives of persistent organic pollutants (POPs).

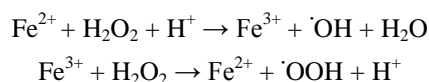
Due to their low solubility in water the substances occur in the aquatic environment more likely in sediments. For this reason, we chose just a sediment for the oxidation of PAH by the Fenton reaction. These substances are abundantly present in sediments of the Černý příkop locality, which is an artificially built drainage channel passing through the territory of the town of Ostrava, in particular through the part of Mariánské Hory. This area is marked by great industrial activity (see Figures 1 and 2)[1,2].



Fig. 1 The Černý příkop locality [foto L. Nezvalová]

2 FENTON REACTION

This is a reaction of ferrous ions and hydrogen peroxide. Reaction products are ferric ion, hydroxyl radical and hydroxyl ion. The hydroxyl radical is a very strong oxidizing agent and attacks many organic substrates. It can decompose organic compounds to water and carbon dioxide.



The hydroxyl radicals are able to degrade the target contaminants by oxidation. The resulting Fe^{3+} ions may further react with H_2O_2 and a hydroxyl radical, which leads to the regeneration of Fe^{2+} [3,4].

2.1 Factors affecting the Fenton reaction

When carrying out the experiments an influence of many factors must be taken into account, affecting the efficiency of the Fenton reaction.

pH

For an optimum course of the reaction pH is in the range of 3 to 5.5. The higher pH, the lower the speed of reaction and thus the degradation process efficiency. The reason is the loss of Fe^{2+} ions in solution caused by their coagulation in the form of $\text{Fe}(\text{OH})_3$. Low pH causes an excessive decomposition of H_2O_2 to oxygen and water.

Temperature

The higher the temperature, the higher the efficiency of the Fenton reaction. At temperatures over 40 °C the decomposition of hydrogen peroxide to oxygen and water occurs (process efficiency decreases).

Ratio $\text{Fe}^{2+}:\text{H}_2\text{O}_2$

It affects the speed of production of OH radicals and their degradation. The higher the peroxide concentration, the higher the speed of reaction. The higher the quantity of Fe^{2+} , the slower the process.

Concentration of inorganic anions

Some anions degrade hydroxyl radicals, or form complex compounds with iron (incapable of further reaction). Examples of such anions are e.g. SO_4^{2-} , Cl^- , HPO_4^{2-} a HCO_3^- [3,4].

3 METHODOLOGY

The Fenton reaction was performed on a sample of sediment from the Černý příkop locality. Sampling of sediments took place according to the applicable standard ČSN ISO 56 67-12 Water quality - sampling - part 12: Guidelines for sampling of bottom sediments. A composite sample was taken into glass sample tubes, which were wrapped in an aluminum foil (preventing the transmission of light and the degradation of PAHs).



Fig. 2 Sampling site, Černý příkop [foto P. Malíková]

After taking the samples the samples were transported to the laboratory of the Institute of Environmental Engineering, which ensured their homogenization, the sampling for initial analysis.

Analyses of sediments were carried out in laboratories of the Centre for Nanotechnology. In individual experiments 30 g of dry matter was used, which is the optimum amount required for the analyses.

3.1 Determination of the dose of hydrogen dioxide

In the first step, it was necessary to determine the optimum dose of hydrogen peroxide. Five glass jars were dosed with an appropriate amount of the homogenized sediment (i.e. 30 g of dry matter). The individual samples were added by different amounts of ferrous sulphate heptahydrate (p.a.) and hydrogen peroxide. The ratio of hydrogen peroxide and ferrous sulphate was 10:1. In order to meet the optimum value of pH of the Fenton reaction sulphuric acid was dosed. Dosing of individual chemicals is shown in Table 1.

Tab. 1 Quantities of reagents for determining the optimum dose of hydrogen peroxide

SAMPLE IDENTIFICATION	DOSE OF $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	DOSE OF H_2O_2
	[g]	[ml]
0	/	0
1	10,00	100
2	20,00	200
3	30,00	300
4	40,00	400
5	50,00	500

The Fenton reaction ran for 6 hours and samples were mixed in mixers with a constant number of revolutions (100 rpm). After this time, samples were filtrated via a vacuum filtration apparatus. The solid phase was transferred into glass sample tubes and analyzed in the Centre for Nanotechnology. The results are shown in Table 4.1.

3.2 Methodology of oxidation of PAHs by the Fenton reaction

In the next part of the experiment, we focused on the effect of the concentration of hydrogen peroxide and mixing time on the efficiency of the Fenton reaction. Based on the results obtained for determining the optimum

dose of hydrogen peroxide the dose of 500 ml of hydrogen peroxide per 30 g of dry matter of sediment was determined for further experiments. This is the amount, by which the lowest concentration of PAHs (the highest efficiency of the Fenton reaction) has been achieved.

Th glass jars were dosed again with the optimum amount of the homogenized sediment (corresponding to 30 g of dry matter). Then different concentrations of hydrogen peroxide were dosed and therewith the corresponding quantity of ferrous sulphate (while maintaining the ratio of $\text{H}_2\text{O}_2:\text{Fe}^{2+}$ 10:1). The mixtures were blended at time intervals of 6, 12 and 24 hours at constant revolutions (100 rpm). Then the samples were filtrated (see Figure 3) and analyzed in laboratories of the Centre for Nanotechnology.

To determine the efficiency of the pure Fenton reaction (without the effect of mixing) we have prepared blank samples, for which the same conditions were observed as for the other samples, however they were not dosed with hydrogen peroxide. The results are shown in Table 4.2.

Tab. 2 Testing of different concentrations of hydrogen peroxide at different time intervals

SAMPLE IDENTIFICAT ION	DOSE OF $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ [g]	DOSE OF H_2O_2 [ml]	REACTION TIME [min]
blank 6h	/	0	360
10% 6h	50,00	500 ml 10%	360
20% 6h	50,00	500 ml 20%	360
30% 6h	50,00	500 ml 30%	360
blank 12h	/	0	720
10% 12 h	50,00	500 ml 10%	720
20% 12h	50,00	500 ml 20%	720
30% 12h	50,00	500 ml 30%	720
blank 24h	/	/	1440
10% 24h	50,00	500 ml 10%	1440
20% 24 h	50,00	500 ml 20%	1440
30% 24 h	50,00	500 ml 30%	1440



Fig. 3 From the left: Filtered crude sediment, filtered sediment after 6 hours of mixing without hydrogen peroxide, filtered sediment after 24 hours of mixing with 30% hydrogen peroxide

4 RESULTS AND DISCUSSION

The following chapters present the results of determining the optimum dose of hydrogen peroxide and the efficiency of the Fenton reaction during the oxidation of Σ PAHs. Σ PAHs involves the following analytes: naphthalene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo (a) anthracene, chrysene, benzo (b) fluoranthene, benzo (k) fluoranthene, benzo (a) pyrene, dibenzo (ah) anthracene, benzo (ghi) perylene and indene (1,2,3-cd) pyrene.4.1.

The optimum dose of hydrogen peroxide

Based on the methodology presented in Chapter 3.1. we set the dose of concentrated hydrogen peroxide to 500 ml. In this volume of hydrogen peroxide the largest number of Σ PAHs was degraded. The decrease of the concentration of polycyclic aromatic hydrocarbons is apparent from Figure 4.

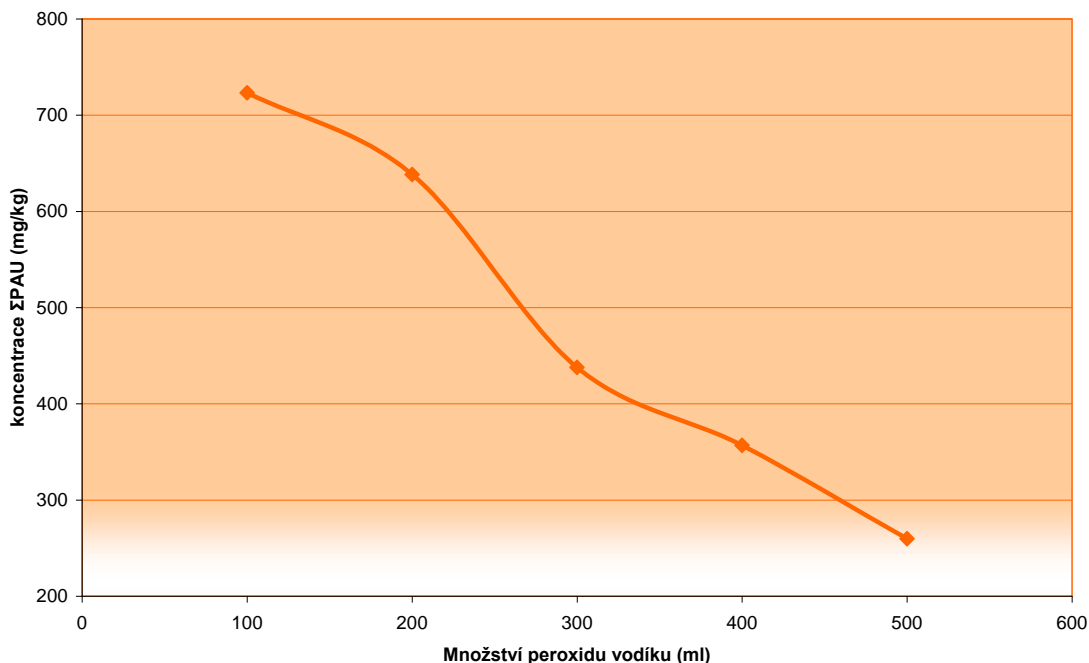


Fig. 4 Dependence of the decrease of Σ PAHs content on the amount of concentrated hydrogen peroxide

4.2 Results of oxidation of the Fenton reaction

In this chapter we deal with the results of the Fenton reaction involving the oxidation of Σ PAHs. From Figure 5 the decrease of the contents of Σ PAHs is obvious depending on the concentration of hydrogen peroxide and then on time. With increasing concentrations of hydrogen peroxide the polycyclic aromatic hydrocarbons oxidized more easily, which is valid also for extending the oxidation time. The best results were achieved when using 30% hydrogen peroxide with the 24-hour reaction time. The efficiency of the Fenton reaction in case of using 30% hydrogen peroxide ranged from 21.22 % (at 6-hour reaction time), 33.69 % (at 12-hour reaction time) up to 50.82 % (at 24-hour reaction time).

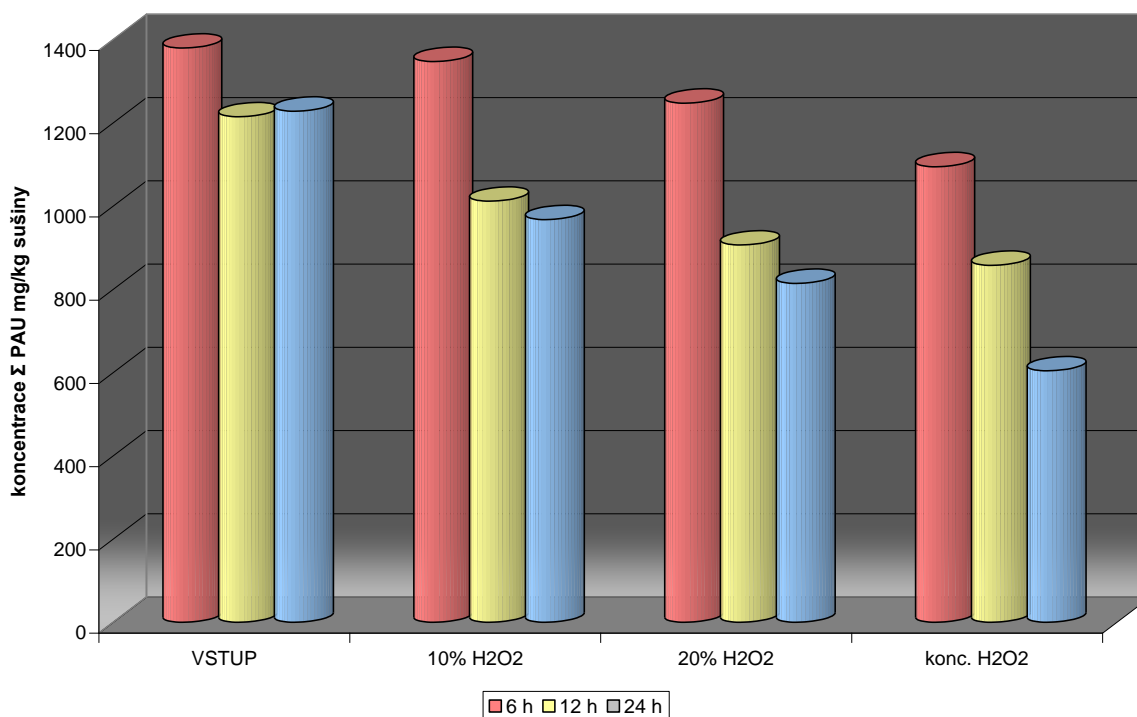


Fig. 5 Decrease of the Σ PAU content per the quantity of hydrogen peroxide

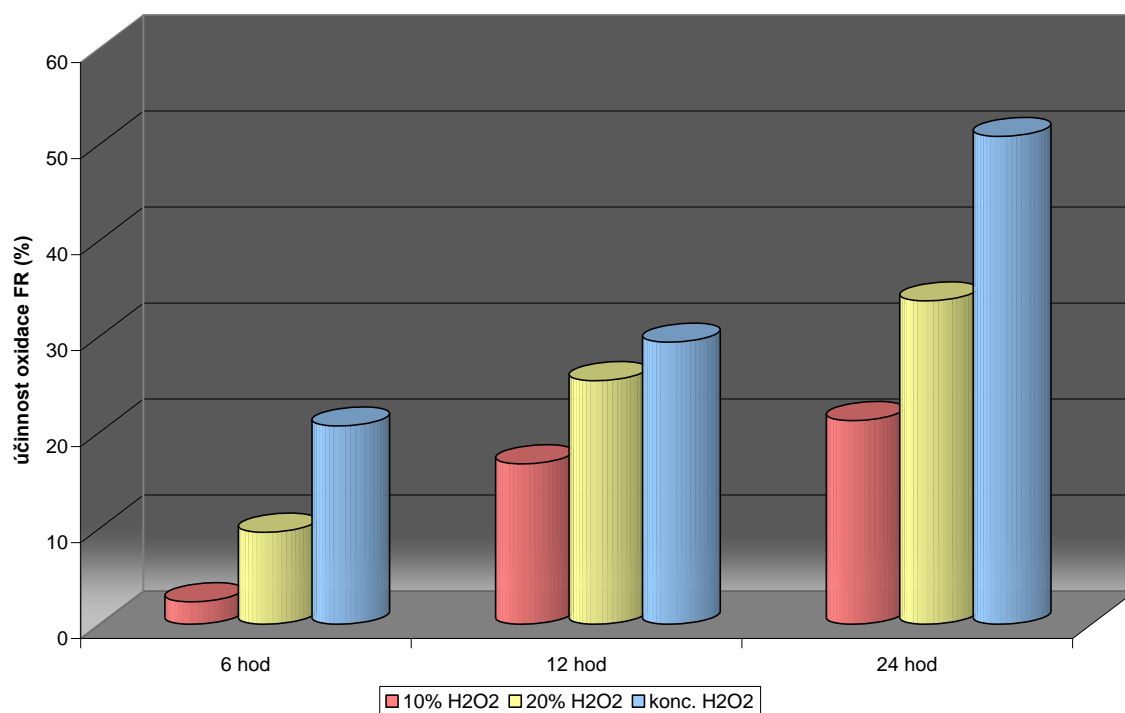


Fig. 6 Efficiency of the Fenton reaction

CONCLUSION

The aim of the presented paper was to verify the effect of the Fenton reaction for degradation of Polycyclic aromatic hydrocarbons in sediments. For experiments a sediment was chosen from the Černý příkop stream, leading to the Odra river. All experiments were performed under laboratory conditions.

The first goal of the experiment was to determine the optimum dose of hydrogen peroxide the oxidation to be effective. It was chosen in the amount of 500 ml. Further part of the experiment was focused on the evaluation of effects of different hydrogen peroxide concentrations and different reaction times on the efficiency of the Fenton reaction. In particular, the concentrations of hydrogen peroxide of 10 %, 20 %, 30 % were chosen. The selected time intervals were - 6 h, 12 h and 24 h. In order to eliminate the degradation by a mere mixing, for all time series input samples were determined (i.e. the sediment mixed for 6 h, 12 h and 24 h without ferrous sulphate and hydrogen peroxide). Thus we could evaluate the efficiency of the pure Fenton reaction. The graphs 5 and 6 show that the higher the concentrations of hydrogen peroxide and the higher interaction time, the higher the efficiency of the Fenton reaction. In case of our experiments performed the highest efficiency was achieved when using 30% hydrogen peroxide. In particular, when using 30% peroxide and 24-hour reaction time the efficiency of the Fenton reaction achieved 50.82%.

Acknowledgement

The work was created under the financial support of the internal doctoral grant IGS 2101/ 546 of the Faculty of Mining and Geology. The authors thereby thank for the support to VSB-TU Ostrava, Faculty of Mining and Geology.

REFERENCES

- [1] HERČÍK, M. Životní prostředí – Úvod do studia. 1. vyd. Ostrava : VŠB – Technická univerzita Ostrava, 2000. 141 s. ISBN 80-7078-340-0.
- [2] LYČKOVÁ Gabriela, aj. Biodegradace PAU, PCB a NEL ve vzorku sedimentů Černého potoka (Česká republika). In FEČKO, Peter; Čablík, Vladimír (ed). *Možnosti zpracování odpadů po důlní a metalurgické činnosti : 1.12. – 2.12.2005, VŠB-TU Ostrava*. Ostrava : VŠB-Technická univerzita Ostrava, 2005. s. 69-72. ISBN 80-248-0949-4.
- [3] VYSKOČILOVÁ J.: Katalytická oxidace DEHP peroxidem vodíku, Diplomová práce Univerzita Tomáše Bati ve Zlíně, 2008.
- [4] PROUSEK, J.; PRIESOLOVA, S. *Practical Utilization of Zero-Valent Iron in Fenton Reaction for Treatment of Coloured Waste Waters*. Chemické listy [online]. **2002**, 96, 893-896 [cit. 2008-11-24]. <Available from www: http://www.chemicke-listy.cz/common/article-vol_96-issue_11-page_893.html>

RESUMÉ

Polycyklické aromatické uhlovodíky jsou látky s rizikovým faktorem nejen na lidské zdraví, ale také na stav životního prostředí. Tyto látky se do životního prostředí dostávají především antropogenní činností, zejména pak průmyslovou činností. Ostrava se řadí k oblastem, které jsou značně ovlivněné různými odvětvími průmyslu. Z tohoto důvodu se zde tato skupina látek vyskytuje v poměrně vysokých koncentracích. Jednou z významných lokalit s vysokým obsahem polycyklických aromatických uhlovodíků jsou sedimenty z vodoteče Černý příkop.

Pro odstranění polycyklických aromatických uhlovodíků z životního prostředí existuje celá řada metod. V tomto článku se zabýváme aplikací Fentonovy reakce při oxidaci polycyklických aromatických uhlovodíků v matrici sedimentu Černého příkopu v laboratorních podmínkách. Experiment byl rozdělen na dva dílčí úkoly, a to na stanovení optimální dávky koncentrovaného peroxidu vodíku a aplikaci Fentonovy reakce na sediment. V druhé části jsme sledovali úbytek obsahu polycyklických aromatických uhlovodíků ve třech časových intervalech.